BIODEGRADABLE FILMS FROM POLY (LACTIC ACID) (PLA)-CHITOSAN-SILVER NANOPARTICLES: PREPARATION AND CHARACTERIZATION

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ABSTRACT

The biodegradable food packaging films were produced from biopolymers poly (lactic acid) (PLA), chitosan, and silver nanoparticles. The objectives of this research are to produce the biodegradable food packaging films from biopolymers poly (lactic acid) (PLA), chitosan, and silver nanoparticles and also to study the effects silver nanoparticles on the antimicrobial qualities of silver nanoparticles loaded with chitosan-PLA based films. Other objective in this research is to study the characterization in chemical, mechanical and biodegradability of biodegradable food packaging films. The characteristics of biodegradable food packaging films were evaluated by using equipments like Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The film also was characterized in term of moisture content and water absorption test and also biodegradability test using soil burial degradation method. The biodegradable food packaging films based of PLA-chitosan loaded with silver nanoparticles also have antimicrobial properties towards any bacteria due to the present of silver nanoparticles that have characteristics of antifungal and antibacterial. In this study, the antimicrobial properties of the films were investigated through the antimicrobial activities by using agar disc diffusion methods and test the films with the microbial *E.coli* bacteria. The performance of films were optimized by manipulating the concentration of silver nanoparticles in order to obtain the biodegradable food packaging films that have high biodegradability and high qualities for food packaging application. The results shows that, the films were show positive response towards degradation process due to the weight loss within 12 days and the poly(lactic acid) (PLA) film show high resistivity towards water compared to the chitosan (CS) film. The concentration of silver nanoparticles at (23.1 % w/w SNP) shows the 100% of inhibition against Gram-negative bacterium *E.coli* and Gram-positive bacterium *Micrococcus.* Thus, it show that silver nanoparticles were successfully inhibit the bacteria grow and improve the antimicrobial properties of poly(lactic acid) (PLA)-loaded chitosan-silver nanoparticles blend films.

BIODEGRADASI FILEM DARIPADA POLI (ASID LAKTIK) (PLA)-CHITOSAN-NANOPARTIKEL PERAK: PENGHASILAN DAN PENCIRIAN

ABSTRAK

Pembungkusan makanan biodegradasi filem dihasilkan dari biopolimer poli (asid laktik) (PLA), chitosan, dan nanopartikel perak. Objektif kajian ini adalah untuk menghasilkan filem pembungkusan makanan terbiodegradasi daripada biopolimer poli (laktik asid) (PLA), chitosan, dan nanopartikel perak dan juga untuk mengkaji kesan nanopartikel perak pada sifat daya tahan terhadap bakteria melalui campuran nanopartikel perak dengan chitosan dan PLA filem. Objektif lain dalam kajian ini adalah untuk mengkaji sifat kimia, mekanikal dan biodegredasi filem pembungkusan makanan terbiodegradasi. Filem pembungkusan makanan terbiodegradasi telah dinilai dan dicirikan dengan menggunakan peralatan seperti spektroskopi jelmaan Fourier inframerah (FTIR) dan mikroskop imbasan elektron (SEM). Makanan terbiodegradasi pembungkusan filem juga dicirikan dalam sifat penyerapan terhadap air melalui kaedah serapan dan biodegredasi menggunakan kaedah kambusan tanah. Terbiodegradasikan filem pembungkusan makanan berasaskan PLA-chitosan sarat dengan nanopartikel perak juga mempunyai ciri-ciri daya tahan terhadap bacteria kerana kehadiran nanopartikel perak yang mempunyai ciri-ciri antikulat dan antibakteria. Sifat antimikrob pada pembungkusan biodegradasi filem makanan berasaskan PLA-chitosan-silver nanopartikel disiasat melalui aktiviti antimikrobial dengan menguji filem dengan bakteria E.coli mikrob. Prestasi filem pembungkusan biodegradasi makanan dioptimumkan dengan memanipulasi kepekatan nanopartikel perak untuk mendapatkan filem pembungkusan makanan terbiodegradasi yang mempunyai biodegredasi yang tinggi. Keputusan menunjukkan filem yang dihasilkan daripada chitosan, PLA dan nanopartikel perak terbiodegradasi dalam masa yang singkat iaitu 12 hari sahaja dan PLA filem menunjukkan daya tahan keserapan air yang tinggi berbanding chitosan filem. Kepekatan nanopartikel perak pada peratus 23.1 menunjukkan seratus peratus perencatan terhadap bakteria positif *E.coli* dan bakteria negatif *Micrococcus*. Ini menunjukkan nanopartikel perak berkesan dalam menjadikan filem mempunyai daya tahan yang tinggi terhadap bakteria.

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LIST OF SYMBOLS

°C	Degree celcius
g	grams
H	hour
L	litre
ml	millilitre
mm	millimetre
min	minutes
w/w	Weight per weight
v/v	Volume per volume
%	Percentage
$\bar{\upsilon}$	wavenumbers
λ	wavelengths

LIST OF ABBREVIATIONS

Ag-nanoparticles	Silver nanoparticles
CH_3COOH	Acetic Acid
CS	Chitosan
DD	Degree Deacetylation
DLS	Dynamic Light Scattering
E.Coli	Escherichia coli
FTIR	Fourier transform infrared spectroscopy
IR	Infrared
PCL	Poly (e-caprolactone)
PEK	Polyethylketone
PGA	Poly (glycolic acid)
PLA	Poly (lactic acid)
PHB	Poly (3-hydroxybutyrate)
PHBV	Polyhydroxyvalerate
PVC	Polyvinyl chloride
PVOH	Polyvinyl alcohol
PVAC	Polyvinyl acetate
SEM	Scanning Electron Microscopy
SNP	Silver nanoparticles
SPR	Surface Plasmon Resonance
UV	Ultra-violet

CHAPTER 1

INTRODUCTION

1.1 Background of Proposed Study

The development of plastics or packaging films based on biopolymers has wide applications due to their environmentally friendly nature and their potential use in the food packaging industry (Marcos *et al.*, 2010). The biodegradable and biocompatible polymers have caused significant attention from both ecological and biological perspectives in the past decade. In general, synthetic polymers produced from petrochemical are not easily degraded in the environment and also contains substances of carcinogen that is an agent directly involved in causing cancer (Momani, 2009).

Packaging films based on biopolymers driving efforts towards biodegradable and biocomposite polymers that can be used as renewable and non-toxic resources. The most popular and important biodegradable polymers are aliphatic polyesters such as poly(lactic acid) (PLA), poly(glycolic acid) (PGA), poly(e-caprolactone) (PCL) and poly(3-hydroxybutyrate) (PHB), and among of them, PLA has received the most attention due to its renewable resources and biocompatibility (Tokiwa *et al.*, 2009).

In addition, due to environmental considerations, the elaboration of new edible or biodegradable bioactive packaging constitutes a very interesting option to recycle. Biodegradation poly(lactic acid) generates acidic degradation products so chitosan may be combined with acid producing biodegradable polymers so that local toxicity due to the acid by products can be reduced (Yao *et al.*, 2003). Chitosan was thus used to produce films from renewable resources and have multipurpose material such as food packaging, drug release component and for environmental pollutants.

Chitin that derived from polysaccharide is a chitosan that is one of the natural polymers and largely widespread in living organisms such as shellfish, shellcrab, insects and mushrooms (Sebastien *et al.,* 2006). Chitosan is monocomponent antimicrobial agent is not already full filling the requirements of some conditions. For instance, the combination of chitosan with other inorganic agents such as Ag, Zn, $SiO_{2,}$ and TiO_2 and among them chitosan-Ag nanoparticles composite had significantly have high antibacterial activity with only small presence of Ag-nanoparticles which exhibit potential antifungal properties (Li *et. al.,* 2010).

1.2 Problem Statement

Recently, the materials of food packaging from the synthetic polymers have become increasingly important due to its high demands and low cost of manufacturing. The increasing of the production of synthetic polymers can cause many environmental problems including waste accumulation and pollutions. Synthetic polymers are not biodegradable and its end up in landfill sites and produce very harmful gases that can cause environmental pollutions and soil contaminations. A synthetic polymer takes a long time to degrade due to the molecular bonds of the polymer makes the polymer so durable and resistant to biodegradation. The burning of synthetic polymer also can release dioxin which highly toxic and will cause chronic disease like cancer through inhalation. Hence, it is very crucial to find other biodegradable polymers that are environmental friendly to nature and will degrade without ends up in landfill by using renewable sources of biodegradable polymer such as poly(lactic acid) (PLA) and chitosan to substitute the using of synthetic polymer.

1.3 Research Objectives

1. To produce the biodegradable of food packaging films from biopolymers poly (lactic acid) (PLA), chitosan, and silver nanoparticles.

2. To investigate the effects of silver nanoparticles on antimicrobial properties of poly(lactic acid) (PLA)-loaded chitosan-silver nanoparticles blend films
3. To study the characterization of poly(lactic) acid (PLA)-loaded chitosan-silver nanoparticles blend films in chemical properties and biodegradability of the films.

1.4 Scope of Proposed Study

To achieve the objective of this research, scopes have been identified

i. Preparations of poly(lactic acid) (PLA)-loaded chitosan-silver nanoparticles blend films
ii. Characterization of poly(lactic acid) (PLA)-loaded chitosan-silver nanoparticles blend films by using Fourier Transforms Infrared Spectroscopy (FTIR), UV-Vis absorption spectrophotometer and Scanning Electron Microscope (SEM).
iii. Characterization of poly(lactic acid) (PLA)-loaded chitosan-silver nanoparticles blend films on antimicrobial properties against Gram-negative bacterium *E.coli* and Gram-positive bacterium *Micrococcus* by using the colony forming count method.
iv. Characterization of poly(lactic acid) (PLA)-loaded chitosan-silver nanoparticles blend films on biodegradability by using soil burial degradation

v. Analyzing the moisture and water absorption of poly(lactic acid) (PLA)-loaded chitosan-silver nanoparticles blend films by using swelling method.

1.5 Significance of Proposed Study

The significant of this study is to produce biodegradable food packaging films from PLA and also modified those biopolymers that made up from PLA with chitosan and silver nanoparticles that have better antimicrobial and chemical properties and biodegradability.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

2.1.1 Plastics and environment

Plastics are synthetic substances consisting very large of molecules that produced by chemical reaction. Plastics are one of the organic polymers that have high molecular weight. They are usually synthetics and almost all of them are made from petroleum. Plastics can be remoulded, extruded or processed into others forms including solid object, film and filaments. The structural molecules of the polymers that are plastics are linked together by chemical bonds. Plastics can be divided into two which are thermosetting or thermoplastics materials. The difference between the thermoplastic and thermosetting is their characteristics. The thermoplastic is flexible and becomes soft when heated and hard when cooled while thermosetting is hard and brittle and cannot be heated and remoulded like thermoplastic when heated (Van *et al,* 2000).

Recently, plastics are widely used because of its properties that easy and low cost of manufacturing and processing. Approximately 140 million tons of synthetic polymers are produced worldwide each year to replace more traditional materials and particularly packaging (Swift & Baciu, 2006). Plastics are manufactured to resist the environmental degradation. Over 60% of plastics wastes are produced by households and most of it as single use packaging. Plastics packaging has a cycle less than year and continuously giving the bad effect to the environment. The growing rate of plastics in industries has lead to the increasing of plastic wastes in landfill (Zhen & Yanful, 2005).The solid waste disposal causes serious problem with billions of tons of waste disposed every year. Landfill used to be one of the main routes of disposal in everywhere but landfill capacity is now dimishing (Moore & Sauders, 1997).

To overcome this problem, the 3R are alternative ways which are reduced, reuse and recycle. The word reduced means the reduction of the amounts of materials entering the waste streams by redesigning patterns of consumption and production. The word reuse means transformation of the materials that are no longer need and make its reusable again. But reuse also has limitations. This is because most the plastics that are used are not redesigned to reuse again due to its impurities and contamination. The most common plastics products are food packaging, disposable diapers, agricultural mulch bags and medical appliances are not suitable to reuse again. Recycling of plastics after used is possible but the plastics product for example plastic bags are rarely to be recycled. The technology of the recycling like collecting and sorting of the plastics is expensive and time-consuming process (Tollinski, 2009)

2.1.2 Polymers used in Biodegradable Packaging

With the growing of the environmental pollution that caused by plastics wastes need immediate resolution. Biodegradable plastics have been intensively studied in recent years. (Khabbaz *et al*, 1998) have been commercialized into several of product such as garbage bags, grocery bags, and waste bags that will decompose in proper ways. Plastic packaging demand will increase more rapidly based on the good opportunity of both flexible and rigid packaging. In rigid plastic packaging, the best opportunities are anticipated for trays, cups and tubes.

2.1.3 Development in Biodegradable Packaging Materials

Over the last three decades, there has been a growing interest in biodegradable polymers. Initial interests were in the fields of medical such as producing degradable fibers for sutures and agriculture for mulch films and controlled pesticide release. In more recent years attention has been focused on the rising concern for the environment. Biodegradable plastics are plastics that can undergo a degradation process known as biodegradation (Scott *et al.*, 2007). Biodegradation of plastics materials are leading to change in its chemical structure caused by biological activity leading to naturally occurring metabolic end products. Rate of biodegradation is determined by standardized test systems. Biodegradable plastics have similar properties of conventional plastics but it can be decomposed by the activity of the microorganisms after disposal to the environment (Tharanathan, 2003).

Biodegradable plastics also can be used in hygiene products, households, agriculture and horticultural products and also in medicine. The production of biodegradable polymers will decreases the solid waste problems and environmental pollutions (Bovea *et al.,* 2003)Biodegradable polymers can be divided into two main categories which are naturally occurring biodegradable polymers and synthetic biodegradable polymers (Bovea *et al.,* 2003). Naturally occurs of biodegradable polymers including polysaccharides such as starch, cellulose and chitin/chitosan. Some polyester such as PLA is also naturally biodegradable polymers (Yu *et al.,* 2006). The most attractive feature of the biopolymer based materials is their total biodegradability. As the result they fit perfectly well in the ecosystems and save the world from the growing ecological pollution caused by non-biodegradable plastics (Garlotta, 2002).

Synthetic biodegradable polymers are usually polymers with hydrolysable backbone and polymers that are sensitive to photodegradation or UV-degradation. Examples of polymers that in the group of polyesters are poly(glycolic) acid, poly(glycolic acid-co-lactic acid), polycaprolactone, polyether-polyurethane and poly(amide-enamide). Some common synthetic biodegradable and its description are listed in Table 2.1 (Garthe & Kowal, 1994).

Table 2.1 Common Synthetic Biodegradable Plastics

Plastic Type	Name	Description
Polyester	Polyglycolic acid (PGA)	Hydrolyzable polyhydroxy acid.
	Polylactic acid (PLA)	Hydrolyzable polyhydroxy acid; polymers derived from fermenting crops and dairy products; compostable.
	Polycaprolactone (PCL)	Hydrolyzable; low softening and melting points; compostable; long time to grade.
	Polyhydroxybutyrate (PHB)	Hydrolyzable; produced as storage material by microorganisms; possibly degrades in aerobic conditions; stiff; brittle; poor solvent resistance.
	Polyhydroxyvalerate (PHBV)	Hydrolyzable copolymer; processes similar to PHB; contains a substances ton increase degradability; melting point; toughness; compostable; low volume and costly production.
Vinyl	Polyvinyl alcohol (PVOH)	Water soluble, dissolve during compositing.
	Polyvinyl acetate (PVAC)	Water soluble, predecessor to PVOH; has shown no significant property loss during compositing tests.
	Polyethylketone (PEK)	Water soluble; derived from PVOH; possibly degrades in aerobic and anaerobic conditions.

(Source: Garthe & Kowal, 1994)

2.2 FILM FORMING MATERIAL

2.2.1 Poly(lactic) acid (PLA)

Poly(lactic acid) belongs to the family of the aliphatic polyesters is most important of the biodegradable polymers such as poly(lactic acid) (PLA), poly(3-hydroxybutylene) (PHB), poly(glycolic acid) (PGA) and poly(e-caprolactone) (PCL) but among of them PLA has received most attention due to its biocompatibility, biodegradation, excellent thermal/mechanical properties and superior transparency of the materials (Urayama *et al.,* 2002). PLA is biodegradable through hydrolytic and enzymatic reaction. PLA is produced from the linear aliphatic thermoplastic polyester and also can be synthesized by condensation polymerization of the lactic acid monomers or by ring-opening polymerizations of monomers that those monomers can be obtained from fermentation of corn, potato, sugar beat and sugar cane (Sawai *et al.*, 2007)

The copolymers of PLA are poly ($_{L}$-lactide) and poly ($_{DL}$-lactide). The amounts of monomers affect the physical properties of PLA such as melting point, degree of crystallinity and the mechanical properties of the PLA (Wu, 2006). High molecular weight of PLA will appear colorless and has glossy looks with properties similar to polystyrene. The amorphous PLA is soluble in most organic solvents such as tetrahydrofuran (THF), chlorinated solvents, benzene, chloroform, and 1, 4-dioxane PLA behaved like thermoplastics and will dispose harmless. PLA is degrade by using simple hydrolysis of the ester bond and does not require the presence of enzymes to catalyze this hydrolysis.

The rate of degradation of PLA will depend on the size and shape of PLA and also the isomer ratio and temperature of hydrolysis. PLA degradation is dependent on the time, temperature and molecular weight (Garlotta, 2002).PLA present one of the renewable biodegradable thermoplastics due to its applications in packaging, textile industry, biomedical field and fibre reinforced composite manufacturing (Gregorova *et al.*, 2011). To enhance the impact resistance of PLA and compete with low cost commodity of polymers, considerable progress has been made by blending the PLA with other biodegradable polymers (Martin & Averous, 2002), For biomedical applications, PLA has weak in high loading bearing application, so it is necessary to incorporate the PLA with reinforced fillers (Bleach *et al.*, 2002). PLA or known as poly(**α**-hydroxy acids) generates acidic degradation products at the implanted site which cause the undesirable tissue reaction (Campus, 2002). The acid by product will lead to the local disturbance due to poor vascularisation in the surrounding tissue but the incorporating the PLA with other biodegradable polymers will reduce the toxicity (Yao *et al.*, 2005).

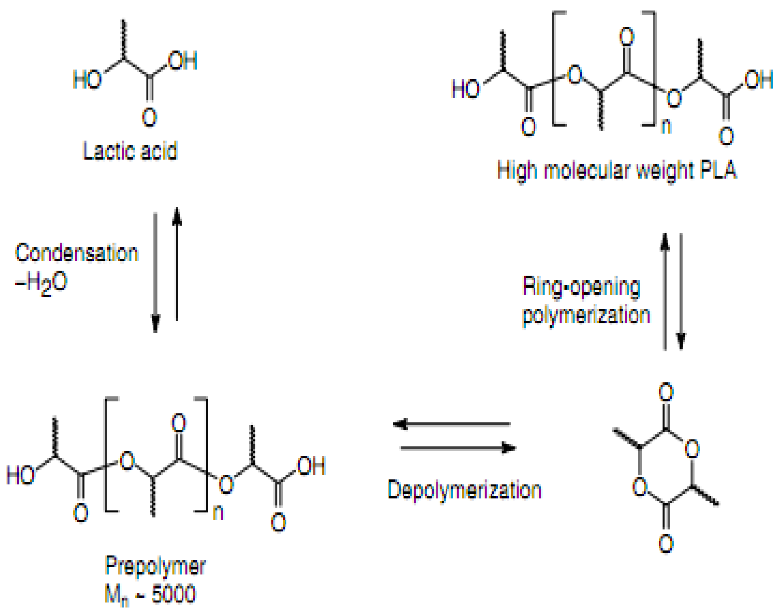

Figure 2.1 Schematic of PLA production via prepolymer and lactide (Gruber *et al.*, 2006)

The synthesis of lactic acid into PLA consists of two different ways as illustrated in Figure 2.1 which are by direct condensation of lactic acid, or ring-opening polymerization of cyclic lactide dimer. The condensation polymerization is low cost but it's difficult in solvent free system in order to obtain high molecular weight. Coupling agents that have been used to increase the molecular weight and the chain-coupling agent will reacts with either hydroxyl or carboxyl groups that leads to different kinetic reaction rates of coupling. Hydroxyl terminated PLA synthesize by condensation of the lactic acid in the presence of the hydroxyl compounds such as glycerol or 1, 4-butanediol which leads hydroxyl ends group by condensation reactions of epoxide to convert to hydroxyl group. And on the others ways is esterification process which has been used to increase the molecular weight of the PLA (Gruber *et al.,* 2006).

Among the various aliphatic degradable polyesters, polylactide (PLA) has been considered as one of the most interesting and promising biodegradable materials and has been used in medical applications, such as surgical implants, culturing of tissue and also closuring wounds (Khang *et al.,* 2003). Polymers of lactic acid are biodegradable thermoplastics poly(lactic acid) (PLA) with low degree of polymerization can help in controlled release or degradable films for large-scale agricultural applications. PLA is commercially and largely scale production due to the remarkable properties that make it suitable for different applications (Averous, 2008).

2.2.2 Chitosan

Chitosan is a linear polysaccharide and biodegradable of copolymer that composed of N-acetyl glucosamine and D-glucosamine. Chitosan is produced by deacetylation of chitin which have the exoskeleton of crustacean's structural element such as crabs and shrimps, (Peesan *et al.,* 2005). Chitosan is a deacetylated product of chitin ß-(1-4)-2-acetamido-2-deoxy-D-glucan. Chitosan has gained attention by researchers due to its functional properties such as film-forming capabilities, mineral binding properties, hypolipidemic activity, biodegradability, antimicrobial activity and acceleration of wound healing (Dutta *et al.,* 2012).

Chitosan is soluble in acidic condition and the free amino group on its polymeric chains contributes to its positive charge (Phaechamud, 2008) and also known to be non-toxic, odourless, biocompatible to animal tissue and biodegradability (Zong *et al.,* 2007). Chitosan is the second most plentiful natural biopolymer and relatively cheap (Dutta *et al.,* 2012). Chitosan has very unique biological properties such as antimicrobial activity and antitumor activity. The antimicrobial activity of chitosan is influenced by species of the bacteria, concentration, pH, solvent and molecular weight of chitosan (Lauzardo *et al.*, 2008). In the antimicrobial action, the binding to the negatively charged wall will destabilize the cell envelope and altered permeability, followed by attachment to DNA with inhibition (Halender *et al.,* 2001). Due to the excellent antimicrobial properties of chitosan, chitosan film may used in food packaging (Triphati *et al.,* 2009).